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New monocationic methylpalladium(II) compounds with several bidentate nitrogen-donor ligands: synthesis, characterisation and reactivity with CO

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Dedicated to Professor Kees Vrieze for his outstanding contribution to the development of coordination chemistry

Abstract

Two series of methylpalladium(II) compounds with mono and bidentate nitrogen-donor ligands, namely $[Pd(N\text{-}N)_2(CH_3)][X]$ (N-N = phen (**1a**), dm-phen (**1b**) (dm-phen = 4,7-dimethyl-1,10-phenanthroline), tm-phen **1c** (tm-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline); X = OTf, PF_6^-) and $[Pd(N\text{-}N)(L)(CH_3)][OTf]$ (N-N = phen and L = py (**1ad**) (py = pyridine), N-N = phen and L = 2-Ph-py (**1ae**) (2-Ph-py = 2-phenyl-pyridine), N-N = phen and L = BzQ (**1af**) (BzQ = 7,8-benzoquinoline), N-N = tm-phen and L = BzQ (**1cf**)), have been synthesised and fully characterised both in solid state and in solution. The crystal structures of $[Pd(phen)_2(CH_3)][PF_6]$ and $[Pd(phen)(2\text{-}Ph\text{-}py)(CH_3)][OTf]$ show a square planar coordination geometry for palladium with the monodentate ligand (one phen molecule plays this role in **1a**) bound to the metal with its plane almost perpendicular to the coordination plane. In both structures the Pd–N bond length *trans* to the methyl is remarkably affected by its *trans* influence. The behaviour in solution is characterised for the first series of compounds by a dynamic process which makes the two N-N ligands equivalent, as corroborated by the ^{15}N NMR analysis: only one averaged signal is shown for all of the four nitrogen atoms. No fluxional process is present for the compounds of the second series, and three main crosspeaks are shown in the ^{15}N–^{1}H HMQC spectra. In particular, the signal of the ^{15}N *trans* to the methyl group has a typical chemical shift, which differs from those of two ^{15}N *trans* to each other. Both series of complexes are reacted with carbon monoxide and the reaction products are studied by ^{1}H NMR spectroscopy and, when possible, by isolating the acyl derivatives. The products of this reaction are affected by the nature of the second molecule of N-ligand. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Nitrogen-donor ligands; Carbon monoxide; Insertion reactions; ^{15}N NMR spectroscopy

1. Introduction

Since the discovery of the oxo-synthesis by Otto Roelen in 1938 [1] the carbon monoxide has found wide application in homogeneous catalysis and the carbonylation reactions, from a more general point of view, represent one of the main topics of organometallic chemistry [2]. They embraces many different types of reactions such as the reductive carbonylation of nitroaromatic compounds to carbamates [3], the oxidative carbonylation of unsaturated substrates [4], the amidocarbonylation [5], the synthesis of acetic acid [6], and the CO/olefin copolymerisation [7].

The study of intimate mechanism of these reactions has received a considerable interest for many years. In this sense, the contribution of Professor Kees Vrieze to this branch of coordination chemistry is widely recog-

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nised, as witnessed quite recently at the occasion of the 25th anniversary of his appointment to the Chair of Inorganic Chemistry at the University of Amsterdam [8].

Among the carbonylation reactions cited above we focused our attention on the CO/olefin co- and terpolymerisation reactions promoted by palladium(II) compounds. In particular, we found that the dicationic bischelated Pd(II) derivatives of general formula [Pd(N-N)(L-L)][PF_6]$_2$ (N-N = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and their substituted derivatives; L-L = N-N or L-L ≠ N-N, therefore L-L = 1,3-bis-(diphenylphosphino)propane (dppp)), are very efficient catalyst precursors for these reactions and the corresponding polyketones are obtained in high yield, with high molecular weight and with negligible decomposition of the active species to palladium metal [9,10]. Unlike the catalytic systems reported in literature [7,11–15], these complexes are characterised by the presence of two molecules of (potentially) chelating ligand in the coordination sphere of the metal centre.

Moreover, up to now all the mechanistic investigations reported for the CO/olefins copolymerisation are based on model systems characterised again by a palladium to ancillary ligand ratio of 1 [16–20]; only one paper has appeared related to the reactivity with CO of organometallic palladium(II) species with two molecules of bidentate ancillary ligand in the coordination sphere of the metal, [Pd(*p*-An-BIAN)(L-L)-(CH_3)][OTf] (*p*-An-BIAN = bis(anisylimino)acenaphthene; L-L = *p*-An-BIAN, phen, 2,9-dimethyl-1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, dppp; OTf = triflate) [21].

One of the questions Professor Vrieze often asked us is "What is the role of the second molecule of nitrogen-donor ligand in the bischelated-Pd(II) system?" With the aim to clarify this aspect we synthesised and characterised two series of monocationic organometallic palladium(II) compounds of general formula [Pd(N-N)$_2$-(CH_3)][X] (N-N = phen (**1a**), dm-phen (**1b**) (dm-phen = 4,7-dimethyl-1,10-phenanthroline), tm-phen (**1c**) (tm-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline); X = OTf, PF_6^-) and [Pd(N-N)(L)(CH_3)][OTf] (N-N = phen and L = py (**1ad**) (py = pyridine), N-N = phen and L = 2-Ph-py (**1ae**) (2-Ph-py = 2-phenyl-pyridine), N-N = phen and L = BzQ (**1af**) (BzQ = 7,8-benzoquinoline), N-N = tm-phen and L = BzQ (**1cf**)). In these two series of complexes two molecules of nitrogen-donor ligand are bound to the same palladium centre: one is always a bidentate ligand, while the other can be either a bidentate or a monodentate one. In this paper we report the synthesis and characterisation of these complexes, together with their reactivity with carbon monoxide.

2. Experimental

2.1. Materials

The nitrogen-donor ligands (Aldrich) together with the analytical grade solvents (Carlo Erba) were used without further purification for synthetic and spectroscopic purposes. The dichloromethane used for the synthesis of complexes was purified through distillation over $CaCl_2$ and stored under inert atmosphere. $Pd(CH_3COO)_2$ was a lone from Johnson Matthey. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

2.2. Instrumentation

IR spectra were recorded in a Perkin–Elmer 983G spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.5 MHz, respectively, in a JEOL EX 400 spectrometer; the resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at 7.26 δ for ^{1}H and 77.0 δ for ^{13}C; CD_2Cl_2 at 5.33 δ for ^{1}H and 53.8 δ for ^{13}C). Two-dimensional correlation spectra (COSY) were obtained with the automatic program of the instrument. The NOE experiments were run with a ^{1}H pulse of 90° of 12.3 μs.

The ^{15}N NMR spectra were recorded using the PFG HMQC sequence [22] in a Bruker DRX 300 spectrometer equipped with a 5 mm triple resonance inverse probe with *z*-gradient, operating at 30.42 MHz ^{15}N frequency, a second 300 W X decoupler giving a 90° ^{15}N pulse of 10 μs. Spectra were recorded without decoupling ^{15}N in f_2, using a spectral width in f_2 (^{1}H) of 10 ppm, an acquisition time of 0.4 s giving a digital resolution of 1.2 Hz per point. In the first experiments up to three values for $J\{^1H, ^{15}N\}$ (2.5, 5 and 8 Hz) were used, these experiments were recorded with a spectral width in f_1 of 500 ppm and 32 increments only. The final experiment was done with a spectral width of 20 ppm (^{15}N) with 256 increments and 16–1024 scans per increment depending on the concentration of the compound. This provided, after linear prediction to 1024, a digital resolution of 0.6 Hz per point. The relaxation delay was 1 s. For experiments using 256 increments and 16 scans, data collection required 2 h. Chemical shifts were referenced to external nitromethane = 0 ppm, negative chemical shifts were reported for lower frequencies. Spectra were recorded at 296 K.

2.3. Synthesis of complexes

All manipulations were carried out in argon atmosphere by using Schlenk techniques and at room temperature, unless otherwise stated.

Elemental analysis (C, H, N), performed by Dr E. Cebulec (Dipartimento di Scienze Chimiche, Trieste,

Italy), were in perfect agreement with the proposed stoichiometry (Tables 1 and 2).

$[Pd(CH_3COO)_2]$, used as a starting material, was transformed in *trans*-$[Pd(PhCN)_2Cl_2]$ following a modified procedure with respect to that reported in the literature [23]. $[Pd(COD)Cl_2]$ was obtained from *trans*-$[Pd(PhCN)_2Cl_2]$ [24]. The synthesis of [Pd(N-N)-(CH_3)Cl] (N-N = phen and its substituted derivatives) from $[Pd(COD)Cl_2]$ was done in analogy to that of [Pd(*p*-An-BIAN)(CH_3)Cl] [25].

2.3.1. Synthesis of trans-$[Pd(PhCN)_2Cl_2]$

$[Pd(CH_3COO)_2]$ (2 g) was dissolved in 60 ml of benzonitrile together with 2.7 ml of hydrochloric acid (37%). The solution was heated to 90 °C for 30 min. To the cooled orange–red solution 35 ml of petrol ether was added and it was filtered over Celite. The product was recovered after 2 days at 277 K. It was filtered under vacuum, washed with petrol ether and dried under vacuum. From the mother liquor another fraction precipitated upon addition of another portion of petrol ether and after 1 week at 277 K. Elemental analysis: C, 44.0; H, 2.54; N, 7.31. Calc. values for $C_{14}H_{10}N_2Cl_2Pd$: C, 43.8; H, 2.62; N, 7.30%.

2.3.2. Synthesis of [Pd(N-N)$(CH_3)(CH_3CN)$][OTf] (N-N = phen, dm-phen, tm-phen)

The compound [Pd(N-N)$(CH_3)(CH_3CN)$][OTf] was synthesised mainly following the method reported in the literature [16b], but with different amount of solvents. In particular, to a suspension of 0.40 mmol of [Pd(N-N)(CH_3)Cl] in 10 ml of dichloromethane a solution of AgOTf (0.46 mmol in 8 ml of anhydrous acetonitrile) was added. After 30 min the AgCl formed is filtrated and the solution obtained is concentrated under vacuum yielding a pale yellow solid upon addition of diethyl ether. The solid is filtered, washed with diethyl ether and dried under vacuum. Average yield: 75%.

Table 1
Elemental analysis for compounds $[Pd(N\text{-}N)_2(CH_3)][OTf]$ (**1a**–**1c**) and [Pd(N-N)(L)(CH_3)][OTf] (**1ad**–**1cf**) [a]

Compound	C (%)	H (%)	N (%)
$[Pd(phen)_2(CH_3)][OTf]$	49.6 (49.5)	2.99 (3.03)	8.87 (8.88)
$[Pd(dm\text{-}phen)_2(CH_3)][OTf]$	52.6 (52.4)	3.94 (3.96)	8.17 (8.15)
$[Pd(tm\text{-}phen)_2(CH_3)][OTf]$	53.2 (54.9)	4.61 (4.75)	7.34 (7.54)
[Pd(phen)(py)(CH_3)][OTf]	41.5 (43.1)	2.87 (3.04)	7.68 (7.93)
[Pd(phen)(2-Ph-py)(CH_3)][OTf]	49.4 (49.6)	3.20 (3.33)	6.92 (6.93)
[Pd(phen)(BzQ)(CH_3)][OTf]·BzQ	49.3 (49.3)	3.60 (3.61)	6.92 (6.92)
[Pd(tm-phen)(BzQ)(CH_3)][OTf]·BzQ	56.5 (61.1)	4.12 (4.31)	6.52 (6.47)

[a] Calculated values are reported in parenthesis.

Table 2
Elemental analysis for compounds $[Pd(N\text{-}N)_2(C(O)CH_3)][OTf]$ (**2a**–**2c**) and [Pd(N-N)(L)$(C(O)CH_3)$][OTf] (**2ad**–**2ae**) [a]

Compound	C (%)	H (%)	N (%)
$[Pd(phen)_2(C(O)CH_3)][OTf]$	49.4 (49.6)	3.20 (3.33)	6.92 (6.93)
$[Pd(dm\text{-}phen)_2(C(O)CH_3)][OTf]$	50.3 (52.1)	3.68 (3.81)	7.52 (7.83)
$[Pd(tm\text{-}phen)_2(C(O)CH_3)][OTf]$	51.1 (54.5)	4.32 (4.57)	6.83 (7.26)
[Pd(phen)(py)$(C(O)CH_3)$][OTf]	41.8 (43.1)	2.71 (2.89)	7.42 (7.53)
[Pd(phen)(2-Ph-py)$(C(O)CH_3)$][OTf]	47.7 (49.3)	3.02 (3.18)	6.59 (6.63)

[a] Calculated values are reported in parenthesis.

2.3.3. Synthesis of $[Pd(N\text{-}N)_2(CH_3)][OTf]$ (N-N = phen (**1a**), dm-phen (**1b**), tm-phen (**1c**))

To a suspension of 0.20 mmol of [Pd(N-N)(CH_3)-(CH_3CN)][OTf] in 20 ml of chloroform, 0.26 mmol of the proper N-N ligand was added (Pd–N-N = 1:1.3), yielding an orange/yellow solution. After 10 min it is filtered over fine paper and concentrated under vacuum to induce precipitation of the product as an orange solid. The solid was removed by filtration, washed with diethyl ether and vacuum dried. Average yield: 80%.

2.3.4. Synthesis of [Pd(phen)(py)(CH_3)][OTf] (**1ad**)

To a suspension of 0.20 mmol of Pd(N-N)(CH_3)-(CH_3CN)][OTf] in 20 ml of dichloromethane, 2.0 mmol of pyridine was added (Pd–py = 1:10), yielding immediately a solution. After 10 min it is filtered over fine paper and concentrated under vacuum to induce precipitation of the product as a white solid. The solid was removed by filtration, washed with diethyl ether and vacuum dried. Average yield: 90%. ^{1}H NMR (CD_2Cl_2, 293 K, δ ppm): 8.97 (dd, 1H, H^2), 8.88 (dt, 2H, H^{α}), 8.70 (dd, 1H, H^4), 8.64 (dd, 1H, H^7), 8.09 (m, 3H, $H^{5,6} + H^{\gamma}$), 8.04 (dd, 1H, H^9), 7.97 (dd, 1H, H^3), 7.87 (dd, 1H, H^8), 7.68 (td, 2H, H^{β}), 1.10 (s, 3H, CH_3).

2.3.5. Synthesis of [Pd(N-N)(L)(CH_3)][OTf] (N-N = phen, L = 2-Ph-py (**1ae**); N-N = phen, L = BzQ (**1af**); N-N = tm-phen, L = BzQ (**1cf**))

The procedure is the same reported above for compound **1ad**, but the solvent used is chloroform instead of dichloromethane. Average yield: 90%. ^{1}H NMR (CD_2Cl_2, 293 K, δ ppm): for **1ae** 9.09 (d, 1H, $H^{6'}$), 8.86 (dd, 1H, H^2), 8.67 (dd, 1H, H^4), 8.60 (dd, 1H, H^7), 8.18 (td, 1H, $H^{4'}$), 8.05 (m, 4H, $H^{5,6} + H^{\beta}$), 8.01 (dd, 1H, H^9), 7.92 (m, 2H, $H^3 + H^{3'}$), 7.82 (dd, 1H, H^8), 7.65 (td, 1H, $H^{5'}$), 7.33 (m, 3H, $H^{\alpha} + H^{\gamma}$), 0.98 (s, 3H, CH_3); for **1af** 12.11 (d, 1H, $H^{10'}$), 9.86 (d, 1H, $H^{2'}$), 9.09 (d, 1H, H^2), 8.76 (d, 1H, H^4), 8.63 (d, 1H, $H^{4'}$), 8.54 (d, 1H, H^7), 8.10–7.55 (signals overlapped: $H^{5,6}$, H^3, H^8, H^9, $H^{9'}$, $H^{8'}$, $H^{7'}$, $H^{6'}$, $H^{5'}$, $H^{3'}$), 1.21 (s, 3H, CH_3); for **1cf** 12.05 (d, 1H, $H^{10'}$), 9.91 (d, 1H, $H^{2'}$), 8.71 (s, 1H, H^2), 8.64 (d, 1H, $H^{4'}$), 8.26 (s, 2H, $H^{5,6}$), 8.04–7.55 (overlapped signals: $H^{9'}$, $H^{8'}$, $H^{7'}$, $H^{6'}$, $H^{5'}$), 7.35 (s, 1H, H^9),

2.87 (s, 3H, $(CH_3)^4$), 2.69 (s, 3H, $(CH_3)^7$), 2.67 (s, 3H, $(CH_3)^3$), 2.20 (s, 3H, $(CH_3)^8$), 1.01 (s, 3H, Pd–CH_3).

*2.3.6. Synthesis of [Pd(N-N)$_2$(C(O)CH$_3$)][OTf] (N-N = phen (**2a**), dm-phen (**2b**), tm-phen (**2c**)) and of [Pd(phen)(L)(C(O)CH$_3$)][OTf] (L = py (**2ad**), L = 2-Ph-py (**2ae**))*

Carbon monoxide was bubbled through a solution of 0.05 mmol of [Pd(N-N)$_2$(CH$_3$)][OTf] or of [Pd(phen)-(L)(CH$_3$)][OTf] in 10 ml of dichloromethane for 20 min, at 273 K. Concentration of the solution and addition of diethyl ether induced the precipitation of the product as a brown solid, that was removed by filtration, washed with diethyl ether and dried under vacuum. The solid must be stored at 277 K. Average yield: 75%. ^{1}H NMR (CD_2Cl_2, 273 K, δ ppm): for **2a** 8.77 (d, 4H, $H^{2,9}$), 8.56 (d, 4H, $H^{4,7}$), 8.08 (s, 4H, $H^{5,6}$), 7.77 (dd, 4H, $H^{3,8}$), 2.34 (s, 3H, CH_3); for **2b** 8.58 (d, 4H, $H^{2,9}$), 8.24 (s, 4H, $H^{5,6}$), 7.55 (d, 4H, $H^{3,8}$), 2.86 (s, 12H, $(CH_3)^{4,7}$), 2.27 (s, 3H, CH_3); for **2c** 8.44 (s, 4H, $H^{2,9}$), 8.22 (s, 4H, $H^{5,6}$), 2.73 (s, 12H, $(CH_3)^{4,7}$), 2.40 (s, 12H, $(CH_3)^{3,8}$), 2.22 (s, 3H, CH_3); at 163 K: for **2ad** 8.95 (d, 2H, H^{α}), 8.70 (d, 1H, H^4), 8.60 (d, 1H, H^7), 8.54 (d, 1H, H^2), 8.12 (t, 1H, H^{γ}), 8.07 (s, 2H, $H^{5,6}$), 7.93 (dd, 1H, H^3), 7.89 (d, 1H, H^9), 7.81 (dd, 1H, H^8), 7.72 (t, 2H, H^{β}), 2.52 (s, 3H, CH_3); for **2ae** 9.33 (d, 1H, $H^{6'}$), 8.67 (m, 2H, $H^{4,7}$), 8.45 (d, 1H, H^2), 8.22 (t, 1H, $H^{5'}$), 8.08 (b, 4H, $H^{5,6} + H^{\beta}$), 7.98–7.80 (b, 4H, $H^{3'} + H^9 + H^8 + H^3$), 7.73 (t, 1H, $H^{4'}$), 7.45 (b, 3H, $H^{\alpha} + H^{\gamma}$), 2.03 (s, 3H, CH_3).

2.4. NMR in situ experiments

The reactivity of both series of complexes, **1a**–**1c** and **1ad**–**1cf**, with CO was investigated in situ by running NMR experiments. CD_2Cl_2 (0.7 ml) was added to a 5 mm NMR tube charged with the complex (7×10^{-3} mmol). After cooling the solution to 273 K, CO was bubbled for 5 min via a needle inserted through a rubber cap into the NMR tube. The sample was placed in a precooled NMR probe and the ^{1}H NMR spectrum was obtained after 15 min.

2.5. X-ray structure determination

Diffraction experiments were carried out at room temperature using the ω–2θ scan technique on a CAD4 Enraf–Nonius single-crystal diffractometer equipped with graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). Throughout the data collection, no noticeable variation in intensity was observed. The reflections were corrected for Lorentz–polarisation effects and for absorption, based on an empirical ψ-scan method. The structures were solved by conventional Patterson [26] and Fourier analyses and refined on F^2 by full-matrix anisotropic least-squares method using the SHELXL-97 package [27]. In the crystal of **1a**, a difference Fourier synthesis revealed the presence of a solvent molecule of chloroform. In **1ae** the triflate anion (disordered over two sites with occupancy of 0.5 each) was refined using a fixed model, leading to an overall structural determination of low accuracy.

All the calculations were performed using the WINGX System, Ver 1.63 [28].

*2.5.1. Crystal data for **1a***

$C_{26}H_{20}Cl_3F_6N_4PPd$, $M = 746.18$, triclinic, space group $P\bar{1}$, $a = 10.887(3)$, $b = 11.781(3)$, $c = 12.421(5)$ Å, $\alpha = 117.37(3)$, $\beta = 95.03(3)$, $\gamma = 92.51(2)°$, $V = 1402.9(8)$ Å^3, $Z = 2$, $\rho_{calc} = 1.766$ g cm^{-3}, μ (Mo Kα) = 1.070 mm^{-1}, $F(000) = 740$. Final $R = 0.0638$, $wR_2 = 0.1176$, $S = 1.021$ for 371 parameters and 5676 reflections, 5423 unique [$R_{int} = 0.0424$], of which 2170 with $I > 2\sigma(I)$, maximum positive and negative peaks in ΔF map 0.398 and -0.652 e Å^{-3}.

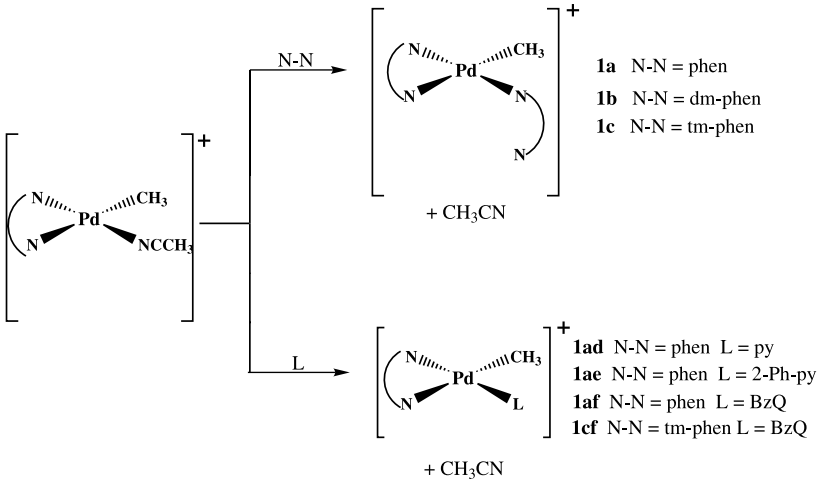
*2.5.2. Crystal data for **1ae***

$C_{25}H_{20}F_3N_3O_3PdS$, $M = 605.90$, monoclinic, space group $C2/c$, $a = 23.842(5)$, $b = 13.855(4)$, $c = 14.971(4)$ Å, $\beta = 98.82(1)°$, $V = 4887(2)$ Å^3, $Z = 8$, $\rho_{calc} = 1.647$ g cm^{-3}, μ (Mo Kα) = 0.901 mm^{-1}, $F(000) = 2432$. Final $R = 0.0785$, $wR_2 = 0.1838$, $S = 1.176$ for 246 parameters and 5005 reflections, 4808 unique [$R_{int} = 0.0671$], of which 1513 with $I > 2\sigma(I)$, maximum positive and negative peaks in ΔF map 0.740 and -0.836 e Å^{-3}.

3. Results and discussion

3.1. Synthesis of complexes [Pd(N-N)$_2$(CH$_3$)][OTf] and [Pd(N-N)(L)(CH$_3$)][OTf]

The synthesis of the two series of complexes [Pd(N-N)$_2$(CH$_3$)][OTf] (**1a**–**1c**) and [Pd(N-N)(L)(CH$_3$)][OTf] (**1ad**–**1cf**), starting from Pd(CH$_3$COO)$_2$, consists of six steps, five of which are reported in the literature for similar derivatives, like [Pd(*p*-An-BIAN)(CH$_3$)-(CH$_3$CN)][OTf] [16b,25] and [Pd(N-N)(CH$_3$)(CH$_3$CN)]-[BAr$'_4$] (N-N = bipy, phen; Ar$'$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) [12a]. The main difference consists in the low solubility of our system, which is instead guaranteed, in the literature systems, by the *p*-An-BIAN ligand in one case and by the particular anion (BAr$'$) in the other. In the complexes studied this problem was overcome by increasing the amount of acetonitrile in the reaction mixture (see Section 2). The desired compounds [Pd(N-N)$_2$(CH$_3$)]-[OTf] and [Pd(N-N)(L)(CH$_3$)][OTf] are easily synthesised from [Pd(N-N)(CH$_3$)(CH$_3$CN)][OTf] through an exchange reaction of the coordinated acetonitrile with a second molecule of the nitrogen-donor ligand (Scheme 1), with the only care to add an excess of the monodentate ligand with respect to palladium



Scheme 1. Synthesis of complexes **1a**–**1cf**.

([L]/[Pd] = 10) for the derivatives **1ad**–**1cf**. In particular, for the [Pd(N-N)(L)(CH_3)][OTf] derivatives this procedure represents a good alternative to the method reported in literature for the compound [Pd(bipy)(γ-picoline)(CH_3)][BF_4] [29].

All the final products are obtained in high yield and high purity. Following the synthetic procedure discussed above and in agreement with the elemental analysis, the complexes with benzoquinoline, **1af** and **1cf**, are always characterised by a BzQ to Pd ratio of 2. When a modified synthetic method was applied ([BzQ]/[Pd] < 10) a non-well defined solid was obtained.

3.2. Characterisation of complexes $[Pd(N\text{-}N)_2(CH_3)][OTf]$ (1a–1c)

The complexes [Pd(N-N)$_2$(CH_3)][OTf] (**1a**–**1c**) were fully characterised both in solid state and in solution.

In order to obtain single crystals suitable for X-ray analysis the replacement of triflate with hexafluorophosphate was necessary and crystals of [Pd(phen)$_2$(CH_3)][PF_6] were directly obtained from the synthesis in chloroform starting from [Pd(phen)(CH_3)(CH_3CN)][PF_6].

The molecular structure of the $[Pd(phen)_2(CH_3)]^+$ cation with the atom labelling scheme is depicted in Fig. 1. The metal displays a slightly distorted square planar geometry with one phen molecule acting as a monodentate ligand, the other one presenting the usual chelating feature and they are practically perpendicular to each other, the best fit planes making a dihedral angle of 89.4(1)°.

The coordination distances for the difunctional base are considerably different (Pd–N(1) 2.036(8), Pd–N(2) 2.115(8) Å), the latter being affected by the *trans* influence exerted by the methyl group. On the other hand, the monodentate phen ligand, unsymmetrically bound to Pd through N(3) (2.040(8) Å), presents the second nitrogen in a pseudo-apical position with respect to the square planar geometry of the metal, at 2.737(8) Å.

Following the rationalisation reported by Vrieze and co-workers [21], which indicate that an axial/equatorial distances ratio higher than 1.3 is distinctive of a square planar coordination rather than a square pyramidal one, we are inclined to indicate the present complex as square planar, although a metal displacement of 0.075(5) Å from the coordination plane towards N(4) (see Fig. 1) should be indicative of a weak interaction between palladium and this nitrogen.

While the Pd–N distances in *trans* positions present values comparable to those of about 2.04 Å found in the bischelated $[Pd(phen)_2]^{2+}$ cations [10b,30], the σ-donor power of the methyl group provides an electron-rich metal centre affecting the value observed for the Pd–N(4) distance, which is longer in comparison with that of 2.674(3) Å, found in the corresponding derivative containing a nitromethyl instead of CH_3 [31].

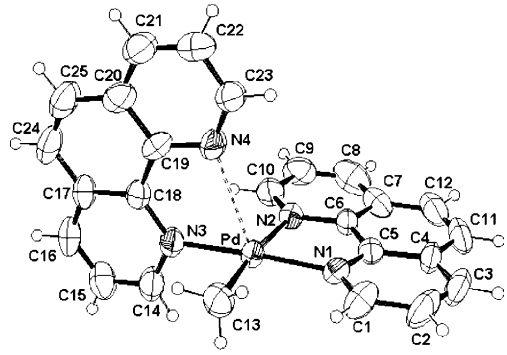


Fig. 1. ORTEP drawing (thermal ellipsoids at 40% probability level) of the cation **1a**. Selected bond lengths (Å) and angles (°): Pd–C(13) 2.018(9); Pd–N(1) 2.036(8); Pd–N(2) 2.115(8); Pd–N(3) 2.040(8); Pd–N(4) 2.737(8); N(1)–Pd–N(2) 80.5(3); N(3)–Pd–N(4) 69.5(3); C(13)–Pd–N(1) 94.4(4); C(13)–Pd–N(2) 173.9(4); C(13)–Pd–N(3) 87.9(4); C(13)–Pd–N(4) 97.6(4); C(14)–N(3)–Pd 116.2(6); C(18)–N(3)–Pd 126.8(6).

Table 3
Relevant ^{1}H, ^{13}C and ^{15}N NMR chemical shifts of complexes **1a**–**1c** and free N-N ligands [a]

Ligand/compound	N-N (^{1}H)				CH_3 (^{13}C)	^{15}N [b] N^1, N^{10}
	$H^{2,9}$	$H^{4,7}$	$H^{5,6}$	$H^{3,8}$		
phen	9.20 (dd)	8.27 (dd)	7.82 (s)	7.65 (q)		−74.4 (8.8)
1a	8.83 (dd)	8.60 (dd)	8.08 (s)	7.83 (dd)	0.93 (s) (0.99)	−123.6 [c]
dm-phen	9.05 (d)		8.04 (s)	7.46 (d)		−77.3 (12.2)
1b	8.67 (d)		8.24 (s)	7.59 (d)	0.82 (s) (0.65)	n.d.
tm-phen	8.93 (s)		8.04 (s)			−78.3 (12.5)
1c	8.55 (s)		8.25 (s)		0.75 (s) (0.35)	−130.8 [c]

[a] Measured at 400 MHz at 20 °C in $CDCl_3$; δ, ppm; s = singlet, d = doublet, dd = double doublet, q = quartet.
[b] Measured at 30.42 MHz at 23 °C in $CDCl_3$; δ, ppm; $^{2}J(^{15}N,^{1}H)$ in parentheses.
[c] Averaged signal (see text).

On the other hand, the Pd–N(4) apical distance agrees with that of 2.714(6) Å, found in the [Pd(*p*-An-BIAN)$_2$(CH$_3$)]$^+$ [21], for the *p*-An-BIAN ligand coordinated in a unidentate fashion.

The Pd–C methyl distance, 2.018(9) Å, is close to those of 2.024(3) and 2.036(6) Å, detected in [Pd(phen)(CH$_3$)((Et)$_2$O)]$^+$ [32] and in [Pd(bipy)(CH$_3$)(γ-picoline)]$^+$ [29] cations, respectively, making allowance for the different e.s.d.

Finally, the crystal packing shows the cations arranged head-to-tail around a symmetry centre with chelating phen stacking at about 3.6 Å.

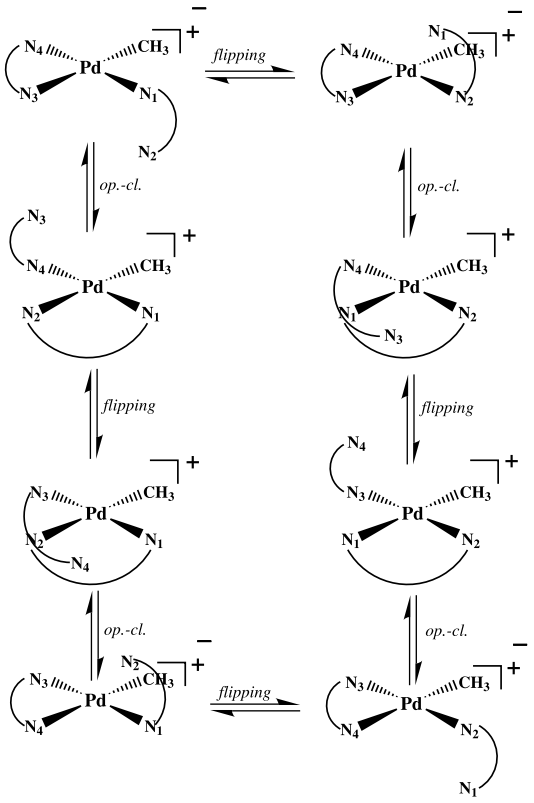
The behaviour in solution for the [Pd(N-N)$_2$(CH$_3$)][OTf] compounds (**1a**–**1c**) was studied by ^{1}H NMR spectroscopy in $CDCl_3$ (Table 3). At room temperature the spectra show, for the nitrogen ligands, four signals integrating for a quarter of the number of chemically equivalent groups, indicating the equivalence of both the two ligands bound to palladium and of the two halves of each ligand. The signal attribution to proton was done in agreement with the literature [30,31]. All the signals are shifted with respect to the free ligand and no signal due to the latter is present. In particular, the resonances of the 'probe-protons' ($H^{2,9}$) are upfield shifted with respect to the same signal in the free ligand. The singlet due to methyl falls in the range between 1.00 and 0.50 ppm in the ^{1}H NMR spectra, and between 1.00 and 0.1 ppm in the ^{13}C NMR spectra. Its chemical shift is upfield-shifted on going from phen to tm-phen. This trend may be related to the electron-donor properties of the ligand, which increase in the same order. The same trend was observed for the signal of the CH_2NO_2 methylenic protons in the complexes [Pd(N-N)$_2$(CH$_2$NO$_2$)][PF$_6$] [31]. Moreover, as already reported for the [Pd(*p*-An-BIAN)(L-L)(CH$_3$)][OTf] compounds [21] and for the nitromethyl derivatives [31], the most important feature in the spectra is the equivalence, in solution, of the two ligands, which appears in contrast with the structure in solid state. The presence of a dynamic process has been demonstrated by recording the spectra at low temperature in CD_2Cl_2, which result in a progressive broadening of the aromatic frequencies. However, even at the lowest temperature reached ($T = 163$ K), the signals are too broad to allow any assignment. After the addition of 1 equiv. of free phen to a solution of [Pd(phen)$_2$(CH$_3$)][OTf] both the signals of coordinated and free phen are shown in the spectrum at room temperature, thus indicating that, if an exchange process with the free ligand is present, its rate is very low on the NMR timescale. Thus, the fluxional process, which renders both of the two molecules of N-N ligand as well as both halves of each of them equivalent, may involve two different equilibria, which alternate to each other: (a) the exchange between the unbound nitrogen atom of the monocoordinated N-N ligand (i.e. N_2) and that of the chelating N-N molecule *trans* to the methyl group (i.e. N_3; *opening–closure*) (Scheme 2); (b) the exchange of the two nitrogen atoms (i.e. N_1 and N_2) at the same coordination site (*flipping*) (Scheme 2). At room temperature, the whole dynamic process is fast on the ^{1}H NMR timescale.

3.3. Characterisation of complexes [Pd(N-N)(L)(CH$_3$)][OTf] (1ad–1cf)

To the best of our knowledge a systematic study of the organometallic Pd(II)-derivatives [Pd(N-N)(L)(CH$_3$)][OTf] (**1ad**–**1cf**), characterised by one bidentate and one monodentate ligand bound to the same palladium centre, has never been reported. As monodentate ligands we chose pyridine (py), as it is the simplest, 2-phenyl-pyridine (2-Ph-py) and 7,8-benzoquinoline (BzQ) since they resemble to 2,2′-bipyridine and to 1,10-phenanthroline, respectively, coordinated in a monodentate fashion to palladium.

The molecular structure of the [Pd(phen)(2-Ph-py)(CH$_3$)]$^+$ cation is shown in Fig. 2. The metal displays a square planar coordination geometry with the phen molecule acting as a chelating ligand. The coordi-

nation distances for **1ae** fall in the expected range for these types of complexes, although the low accuracy of crystallographic data does not allow a detailed analysis. However, the geometrical features of the 2-Ph-py coordination deserve a comment. The 2-Ph-py ligand exhibits a tilted conformation with a N(3)–C(18)–C(19)–C(20) torsion angle of 41(2)°, which excludes any conjugation between the rings. The mean plane through the py ring forms an angle of 64.2(4)° with that of phenanthroline, an orientation remarkably distorted from the expected ideal value of 90°, but close to 62.1° found in the γ-picoline derivative [29]. This conformation, likely dictated by packing forces, does not prevent the py ring to affect the magnetic behaviour of H^9 (Fig. 2, see below).



Scheme 2. Proposed mechanism for the exchange process of complexes **1a**–**1c**.

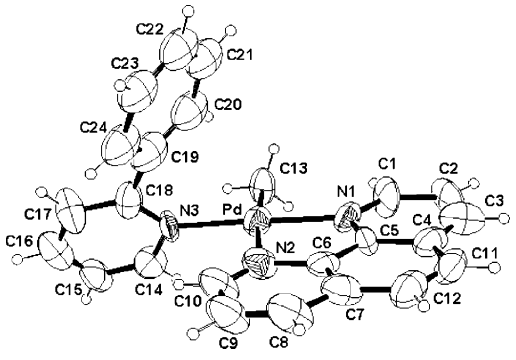


Fig. 2. ORTEP drawing (thermal ellipsoids at 40% probability level) of the cation **1ae**. Selected bond lengths (Å) and angles (°): Pd–C(13) 2.048(12); Pd–N(1) 2.096(13); Pd–N(2) 2.110(14); Pd–N(3) 2.078(11); C(13)–Pd–N(1) 93.0(6); C(13)–Pd–N(2) 174.7(6); N(1)–Pd–N(2) 82.2(6); C(13)–Pd–N(3) 88.2(5); N(3)–Pd–N(1) 178.7(5); N(3)–Pd–N(2) 96.6(6); C(14)–N(3)–Pd 119.1(12); C(18)–N(3)–Pd 122.3(11).

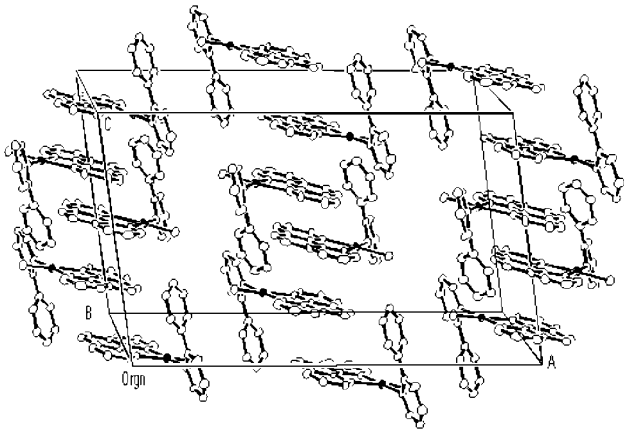


Fig. 3. Perspective view of the crystal packing of **1ae** (triflate anions are not shown for sake of clarity).

In the crystal the cations, piled along the crystallographic *c* axis, are related alternatively by a symmetry centre and a two-fold axis, in such a way to allow the chelating phen to stack at about 3.5 Å (Fig. 3).

The characterisation in solution of this series of complexes was done by mono- and bidimensional ^1H and ^{15}N NMR spectroscopy (Table 4; numbering scheme is reported in Scheme 3).

The spectra of the four derivatives **1ad**–**1cf** share some common features: (i) the ratio between phen and the coordinated L ligand is 1; (ii) the most significant resonances of the two ligands are well separated allowing a clear assignment to the corresponding protons by means of simple COSY experiments. In particular, the number of signals of phen and their integration confirm that phenanthroline is bound to palladium in a non-symmetrical chemical environment and it is not involved in any dynamic process. No signals due to the free ligands, either N-N or L, are present. The protons of the methyl group generate a singlet in a narrow range of frequencies. Thanks to their NOE effect, it is possible to assign the signal of H^2 (Table 4) and starting from it all of the other N–N ligand resonances. Again through an NOE experiment it is possible to distinguish between the frequency of H^7 (NOE with $H^{5,6}$) and H^9. For all the four complexes, the signal of H^9 is remarkably upfield shifted (more than 1 ppm) with respect to the same signal in the free ligand, in agreement with the fact that H^9 falls in the shielding cone of the aromatic nitrogen ligand in *cis* position to it, as clearly evidenced by the crystal structure of **1ae**

(Fig. 2). This shift, already observed for the Pd–(γ-picoline) compound [29], confirms that in **1ad**–**1cf** the monodentate ligand is bound to palladium with its plane non-coplanar with the coordination plane. Moreover, in the case of pyridine the square-planar coordination plane represents a plane of symmetry, too.

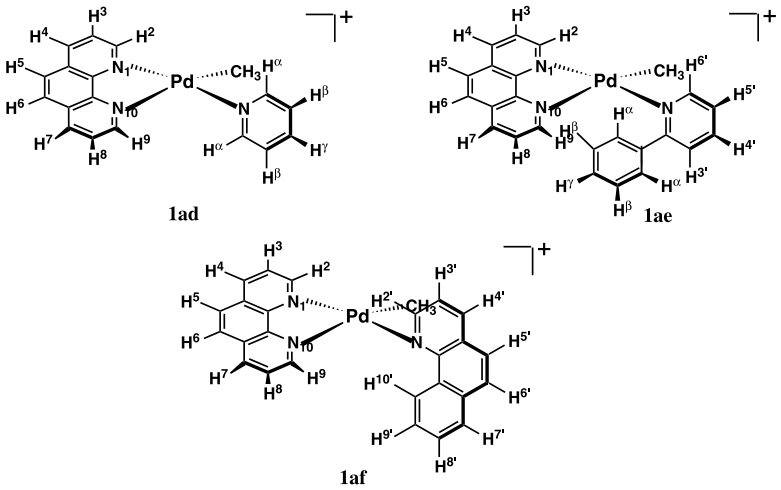
Some differences should be noted between the spectra of **1ad**, **1ae** and those of complexes with benzoquinoline, **1af** and **1cf**. Since the aromatic region of the spectrum of [Pd(phen)(BzQ)(CH_3)][OTf]·BzQ is very crowded, the derivative with tm-phen was synthesised and its signals were easily attributed through NOE experiments performed by irradiating the frequencies of the different methyl groups. The number of signals of benzoquinoline and their integration evidence the presence of two molecules of BzQ for each molecule of N-N ligand, a result in agreement with the stoichiometry of the complexes derived by the elemental analyses (Table 1). On comparison with the spectrum of free benzoquinoline, one set of signals was attributed to the latter, while the other resonances are due to the ligand bound to palladium. Among its several signals, those related to the protons of the heterocyclic aromatic ring ($H^{2'}$, $H^{3'}$ and $H^{4'}$) are shifted to high frequency with respect to the free ligand and they are apparently unaffected by the nature of the N-N ligand. In both complexes **1af** and **1cf** the frequency at the lowest field is the doublet around 12.00 ppm (12.11 ppm for **1af** and 12.05 ppm for **1cf**) with a coordination-induced shifts (CIS) value of almost 2.75 ppm. This signal is attributed to $H^{10'}$ (see Scheme 3). Studies on [Pd(dmp)(L)(OH_2)][ClO_4] (dmp = *N*,*N*-dimethyl-benzylamine; L = 8-methylquinoline, 7,8-benzoquinoline) and on *trans*-[$PtCl_2$-(BzQ)(PX_3)] (X = Et, Ph, Tol) evidence that a downfield shift of the $H^{10'}$ signal of more than 1 ppm is indicative of a weak interaction M ← H–C [33]. Therefore, in agreement with the literature, the coordinated benzoquinoline has the hydrogen atom ($H^{10'}$) approaching the palladium centre and its plane is perpendicular to the coordination plane, which is no more a plane of symmetry. The above results indicate that no metallation process occurs on the benzoquinoline, which behaves like a real monodentate ligand.

Moreover, when a saturation transfer experiment is run by irradiating the signal due to $H^{10'}$ of the bound ligand a clear decrease in intensity was observed for the

Table 4
Relevant ^1H and ^{15}N NMR data for the compounds [Pd(N-N)(L)(CH_3)][OTf] (**1ad**–**1cf**) [a]

Compound	N-N		CH_3	^{15}N [b]		
	H^2	H^9		N^1	N^{10}	N^L
1ad	8.97 (dd)	8.04 (dd)	1.10 (s)	−155.7 (−81.3)	−120.3 (−45.9)	−142.7 (−77.0)
1ae	8.86 (dd)	8.01 (dd)	0.98 (s)	−155.9 (−81.5)	−121.2 (−46.8)	−141.9 (−66.9)
1af	9.09 (dd)	7.45 [c]	1.21 (s)	−157.6 (−83.2)	−121.5 (−47.1)	−155.9 (−79.1) [d]
1cf	8.71 (s)	7.35 (s)	1.01 (s)	n.d.	n.d.	n.d.

[a] Measured at 400 MHz at 293 K in CD_2Cl_2; δ, ppm; s = singlet, d = doublet, dd = double doublet, q = quartet.
[b] Measured at 30.42 MHz at 296 K in CD_2Cl_2; δ, ppm; CIS values in parenthesis.
[c] Overlapped to other signals (see Section 2).
[d] Associated BzQ −75.5 ppm.



Scheme 3. Numbering scheme for complexes **1ad**–**1cf**.

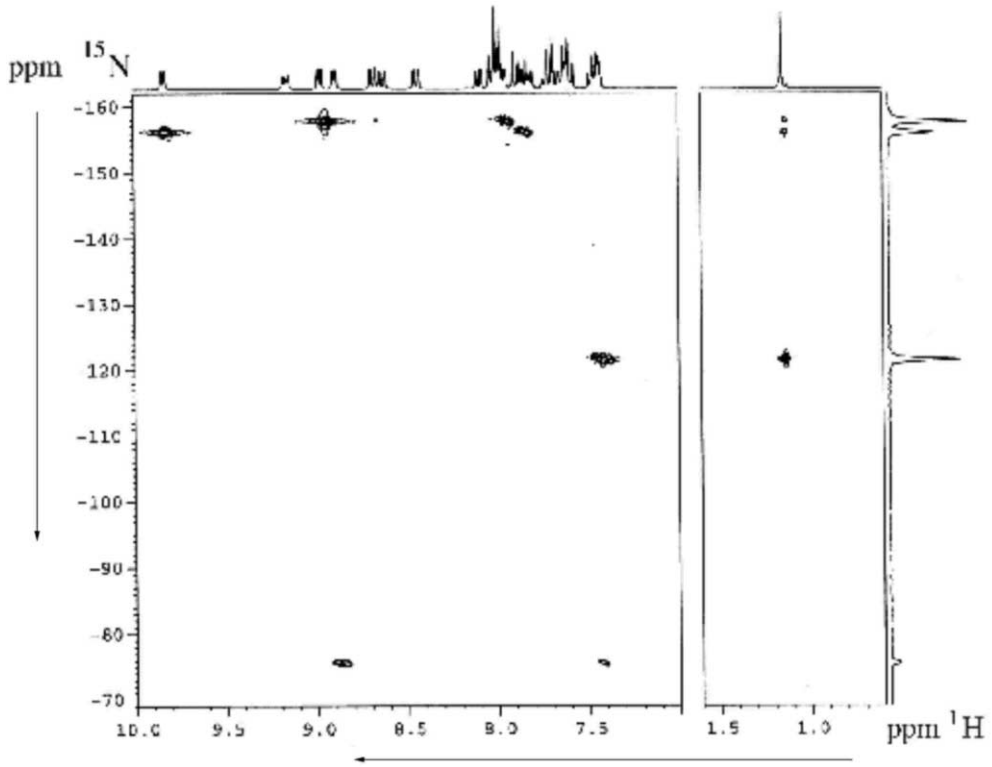


Fig. 4. $^{1}H,^{15}N$-HMQC NMR spectrum of compound **1af**, recorded in CD_2Cl_2 at 296 K.

same signal of the free BzQ. An analogous result was obtained upon irradiation of the frequency of $H^{2'}$ for bound BzQ, indicating that the coordinated and the unbound benzoquinoline are in slow exchange on the ^{1}H NMR timescale at room temperature.

3.4. PFG $^{1}H,^{15}N$-HMQC

In order to substantiate whether or not the various N-ligands in compounds **1a**–**1c** and **1ad**–**1af** are coordinated to palladium, we have acquired their PFG $\{^{1}H,^{15}N\}$-HMQC NMR spectra, at natural abundance of the ^{15}N isotope. The nuclear properties of ^{15}N, i.e. its very low abundance and its rather low and negative gyromagnetic ratio, render acquisition of ^{15}N data employing the PFG $\{^{1}H,^{15}N\}$-HMQC scheme the method of choice, provided a suitable $^{n}J(^{15}N,^{1}H)$ is present. For the compounds studied, the required scalar coupling is indeed available; $^{2}J(^{15}N,^{1}H)$ ranging from about 8 to about 14 Hz for the free N-ligands employed in this study and having unknown but probably reasonable values for their respective palladium compounds. Additionally, a small but distinct $^{3}J(^{15}N,^{1}H)$ was expected between the protons of the methyl group at Pd and the ^{15}N nucleus in *trans* position. The expected crosspeak due to the latter coupling should be an aid in assigning the observed ^{15}N resonances. Since the exact values of $^{2}J(^{15}N,^{1}H)$ in the complexes were unknown, the PFG-HMQC spectra for one of the compounds was first run at several input values of this parameter, which were subsequently used for the other experiments (see Section 2).

The ^{15}N NMR data and CIS have been compiled in Tables 3 and 4. The data were first obtained using a delay corresponding to $J(^{15}N,^{1}H) = 2.5$ Hz. For most compounds, all relevant $^{15}N,^{1}H$ crosspeaks were observed. In some cases, additional recording using a delay corresponding to $J(^{15}N,^{1}H) = 5$ or 8 Hz, emphasising crosspeaks due to some of the larger couplings, gave complementary results.

The ^{15}N chemical shifts of N^{1} and N^{10} of compounds **1ad**–**1af** were attributed by their correlations with H^{2} and H^{9}, respectively, in the HMQC spectra. Also, clear correlations due to $^{3}J(^{15}N,^{1}H)$ of H^{3} and H^{8} and even in some cases with H^{4} and H^{7} were observed. Moreover, an additional crosspeak with Pd–CH_3 was observed for each compound, further substantiating the attribution of the ^{15}N signal due to the *trans*-disposed N^{10}. As an example, the $^{1}H,^{15}N$-HMQC spectrum of **1af** is shown (Fig. 4).

Concerning compounds **1ad**–**1af**, it is seen from Table 4 that the nuclei N^{1} and N^{L} have ^{15}N chemical shifts between -142 and -157 ppm, but the resonance of N^{10} is found at higher frequencies, around -120 ppm. All ^{15}N resonances fall within the expected chemical shift ranges, which were estimated prior to

Table 5
^{1}H NMR chemical shifts for methyl group of compounds [Pd(N-N)$_2$(R)][OTf] (**1a**–**2c**) and [Pd(N-N)(L)(R)][OTf] (**1ad**–**2ae**) (R = CH_3, $C(O)CH_3$) and values of ν(CO) in cm^{-1} [a]

Compound	CH_3	$C(O)CH_3$	$\Delta\delta$	ν(CO)
[Pd(phen)$_2$(R)][OTf]	0.93	2.34	1.41	1686
[Pd(dm-phen)$_2$(R)][OTf]	0.82	2.27	1.45	1687
[Pd(tm-phen)$_2$(R)][OTf]	0.75	2.22	1.47	1681
[Pd(phen)(py)(R)][OTf]	1.11	2.51	1.40	1691
[Pd(phen)(2-Ph-py)(R)][OTf]	1.00	2.20	1.20	1686
[Pd(phen)(BzQ)(R)][OTf]·BzQ	1.18	2.97	1.79	n.d.
[Pd(tm-phen)(BzQ)(R)][OTf] ·BzQ	1.01	3.03	2.02	n.d.

[a] NMR spectra recorded at 400 MHz at 293 K in CD_2Cl_2; IR spectra recorded in KBr pellets.

measurement from the known ^{15}N chemical shifts of the ligands and their approximate CIS values (-75 to -90 ppm for N *trans* to N, -40 to -50 ppm for N *trans* to C) based on previously obtained data, for e.g. $[Pd(CH_3)(N\text{-}N\text{-}N)]^+$ (N-N-N = 2-(2-((2′-pyridylmethylene)amino)ethyl)pyridine) [25], $Pd(CH_3)_2$(Ar-BIAN) [34], and [Pd(*p*-An-BIAN)(L-L)$(CH_3)]^+$ [21]. Indeed, except for N^L of **1ae**, the CIS for N^1 and N^L in these compounds amounts to approximately -80 ppm and for N^{10} the CIS is about -47 ppm.

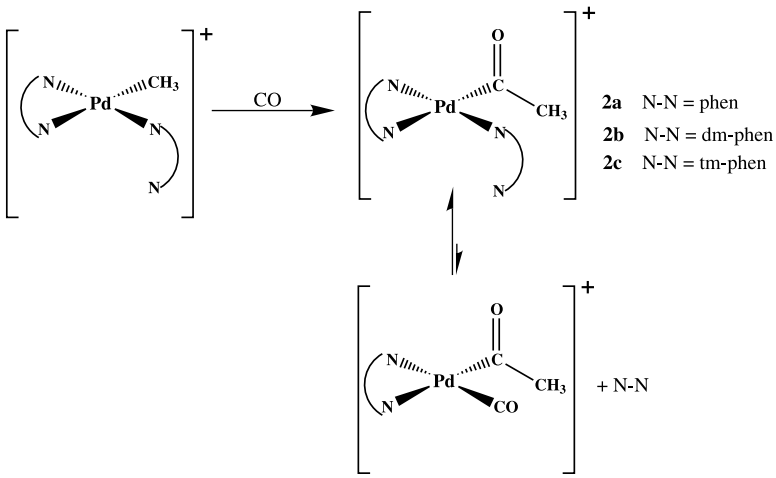
The second BzQ ligand present in compound **1af** is not coordinated, since it gave a ^{15}N resonance correlating to H^2 and H^3 of this ligand at -75.5 ppm (see Fig. 4), which differs only slightly from the value (-76.8 ppm) for the pure BzQ ligand in the same solvent. The exchange process between the free and the unbound BzQ, witnessed by saturation transfer experiments on the ^{1}H NMR timescale (see Section 3.3), was not observable on the ^{15}N NMR timescale.

Compounds **1a** and **1c** both exhibit averaged ^{15}N signals, which are observed at -123.6 and -130.5 ppm, respectively (Table 3). Apparently, all N-atoms of the respective bidentate N-ligands are in fast exchange on the ^{15}N NMR as well as on the ^{1}H NMR timescale (see also above), and the equilibria reported in Scheme 2 account for the complete equivalence of the four nitrogen atoms of the two N-N ligands. The chemical shifts observed are indeed very close to the calculated values, which can be obtained from estimates of the chemical shifts of the individual N-atoms, which are in turn based on the shifts of the free ligands (Table 3) and the CIS values observed for **1ad**–**1af** (Table 4). Estimated values, being the average of the expected ^{15}N shifts of the four N-atoms belonging to one bidentate and one monodentate coordinated phenanthroline (-156, -121, -156 and -75 ppm) and analogously for tetra-methyl-phenanthroline (-161, -125, -161 and -78 ppm), amount to -127 ppm for **1a** and -131 ppm for **1c**. These values are very close to the data observed for **1a** and **1c** and corroborate that indeed exchange of all four nitrogen atoms of the two bidentate ligands in these complexes occurs.

3.5. Reactivity with carbon monoxide

All the complexes of both series were treated with carbon monoxide and the reactions were studied both by ^{1}H NMR spectroscopy and by isolating the insertion products, when possible.

When carbon monoxide was bubbled through a solution of [Pd(N-N)$_2$(CH$_3$)][OTf] (**1a**–**1c**), in CD_2Cl_2, at 273 K, in the ^{1}H NMR spectra, recorded after 15 min, the singlet of the methyl group of the precursor is not present anymore and it is substituted by a new signal at higher frequency (Table 5). In agreement with the literature [21], a downfield shift of 1.4 ppm with respect to the methyl signal of the precursor is indicative of the CO insertion in the palladium–methyl bond, yielding the palladium–acyl derivative [Pd(N-N)$_2$(C(O)CH$_3$)]-[OTf] (**2a**–**2c**) (Scheme 4). This is also confirmed by the



Scheme 4. Reaction scheme of complexes **1a**–**1c** with CO.

strong CO stretching band at 1693 cm^{-1} present in the IR spectrum recorded in dichloromethane solution. The protons of N-N ligands generate four signals integrating for a quarter of the number of chemically equivalent groups, indicating that the equivalence of the nitrogen ligand, observed in the precursor, is retained in the acyl derivative. The only difference with respect to the precursor is the upfield shift ($\Delta\delta = 0.1$ ppm) of the signal due to $H^{2,9}$, which is also quite broad at 273 K. Lowering the temperature, up to 163 K, results only in a progressive broadening of the signals and no attribution signal to proton was possible. Under our reaction conditions, no difference in the rate of CO insertion could be observed on going from phen to tm-phen, as well as no effect of the amount of N-N ligand was evidenced by addition of increasing amounts of free phen (1, 2, 4 and 8 equiv.) either before or after gas bubbling. Moreover, the spectrum of the solution obtained in the presence of 1 equiv. of free phen and CO shows the broad signals of the free ligand, indicating the existence of an exchange process between the coordinated and the free ligand, as confirmed also by a saturation transfer experiment. The rate of this equilibrium is low on the NMR timescale.

Therefore, on the basis of these results it is reasonable to assume that the acyl derivatives $[Pd(N\text{-}N)_2(C(O)CH_3)][OTf]$ are involved in the same fluxional processes already discussed for the precursors $[Pd(N\text{-}N)_2(CH_3)][OTf]$. However, the presence in solution of an exchange equilibrium between the monodentate N-N ligand and CO for the fourth coordination site, giving the acyl-carbonyl species $[Pd(N\text{-}N)(C(O)CH_3)(CO)][OTf]$, cannot be ruled out (Scheme 4). The $[Pd(N\text{-}N)(C(O)CH_3)(CO)]^+$ species has been already reported and characterised, even by X-ray analysis, by Brookhart and co-workers [17]; whereas its formation was not mentioned in the study of the reactivity of $[Pd(p\text{-An-BIAN})(L\text{-}L)(CH_3)][OTf]$ complexes with CO [21].

The palladium–acyl derivatives **2a**–**2c** were isolated by bubbling CO in a dichloromethane solution of $[Pd(N\text{-}N)_2(CH_3)][OTf]$ at 273 K (see Section 2). Their ^1H NMR spectra show the same signals obtained in the in situ NMR experiments.

The carbonylation reaction on the compounds $[Pd(N\text{-}N)(L)(CH_3)][OTf]$ (**1ad**–**1cf**) needs to be discussed separately depending on the L ligand.

When L is the pyridine, the spectrum recorded after 15 min from the treatment with CO shows the methyl signal shifted at higher frequencies of 1.4 ppm with respect to the Pd–CH_3 precursor, indicating the formation of the Pd–acyl species $[Pd(phen)(py)(C(O)CH_3)][OTf]$ (Table 5). The signals in the aromatic region of the spectrum, at 273 K, are broad, but, unlike **2a**–**2c** complexes, they become better resolved on lowering the temperature, reaching a complete decoalescence at 163 K, which allows a clear attribution signal to the aromatic protons through a COSY experiment. It should be noted that both the signals of H^2 and H^9 are shifted to low frequency with respect to the precursor, and the signal related to H^9 is at lower frequency due to the shielding cone of the pyridine *cis* to it. The signal of the methyl is apparently unaffected by variation of temperature. Moreover, at 163 K no signal due to free phen or py is present nor are any other minor signals visible. These data suggest that the broadening of the signals at 273 K may be due to a dynamic process involving the N-N ligand, while not involving the equilibrium between the acyl $[Pd(phen)(py)(C(O)CH_3)]^+$ and the acyl–carbonyl species $[Pd(phen)(CO)(C(O)CH_3)]^+$.

When the compound $[Pd(phen)(2\text{-Ph-py})(CH_3)][OTf]$ (**1ae**) is reacted with CO, in the spectrum at 273 K, the methyl signal, at 2.20 ppm, is shifted to higher frequencies by 1.20 ppm (Table 5) and it is broad as well as the resonances of the aromatic protons (Fig. 5). The band shape analysis performed by decreasing the temperature up to 163 K shows changes for the signals of both the aromatic protons and the methyl (Fig. 5). At 163 K the decoalescence is reached, as for the pyridine derivative, but at this temperature in the aromatic region there are two sets of signals, one of which of very low intensity. Also the signal of the methyl is split into two resonances, at 2.03 and 2.95 ppm, with a 6.25:1 ratio. In agreement with the literature [17], the singlet at 2.95 ppm is attributed to the acyl–carbonyl species $[Pd(phen)(CO)(C(O)CH_3)]^+$, while the other one is assigned to the acyl derivative $[Pd(phen)(2\text{-Phpy})(C(O)CH_3)]^+$. With regard to the aromatic protons region, the main resonances, corresponding to the acyl derivative, were attributed through a COSY experiment and, as already observed for the pyridine derivative, both the signals of H^2 and H^9 are shifted to lower frequencies with respect to the Pd–CH_3 precursor. Therefore, the reaction of the 2-Ph-py derivative with CO gives rise to the equilibrium between the acyl species and the acyl–carbonyl one, whose rate, at room temperature, is intermediate on the ^1H NMR timescale. This equilibrium is considerably shifted towards the acyl derivative $[Pd(phen)(2\text{-Ph-py})(C(O)CH_3)]^+$.

Finally, when both the compounds with the 7,8-benzoquinoline, $[Pd(phen)(BzQ)(CH_3)][OTf]\cdot BzQ$ (**1af**) and $[Pd(tm\text{-}phen)(BzQ)(CH_3)][OTf]\cdot BzQ$ (**1cf**), are reacted with CO, the shift of the methyl signal to higher frequencies amounts to about 2.00 ppm (1.80 ppm for **1af** and 2.02 ppm for **1cf**; Table 5), which is much higher than in the case of **1ad** and **1ae**. The resonances of the aromatic protons are quite broad and, in particular for **1af** those of phen correspond to that of $[Pd(phen)(CO)(C(O)CH_3)]^+$ [17]. Moreover, in the case of **1cf** the signals of BzQ correspond exactly to those of free ligand. Therefore, the reaction of the BzQ derivatives with CO leads to the acyl–carbonyl species [Pd(N-

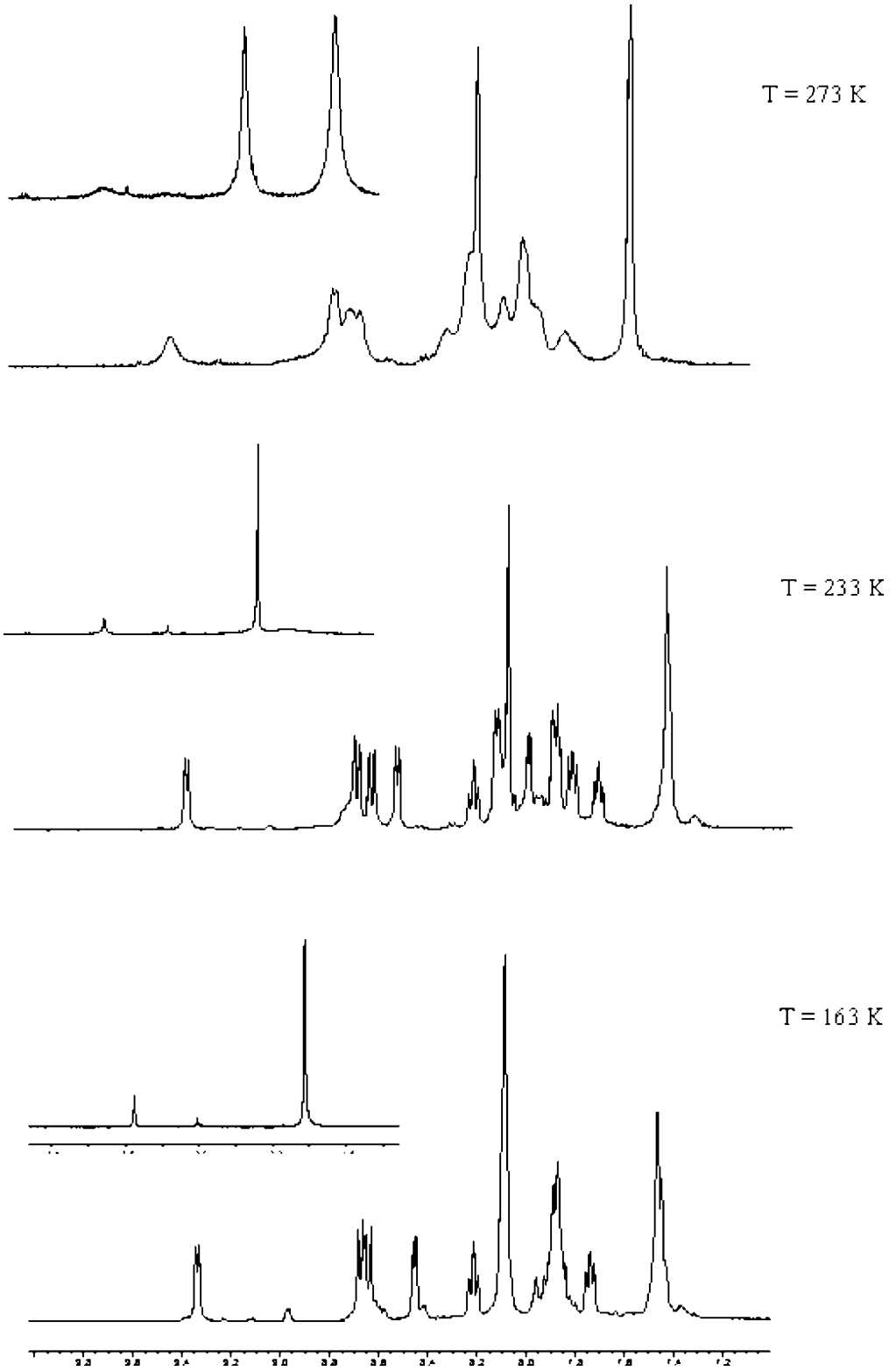
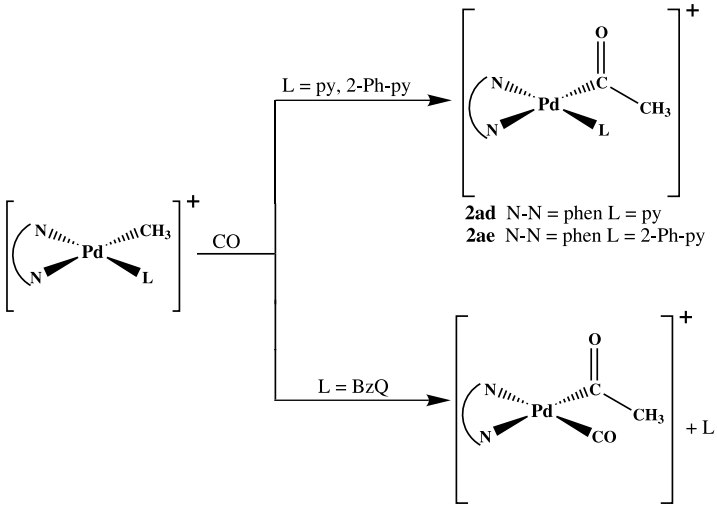


Fig. 5. ^{1}H NMR spectra in CD_2Cl_2 for the system [Pd(phen)(2-Ph-py)(CH_3)][OTf] + CO: variation with temperature; region of signals of aromatic protons and of CH_3 group.



Scheme 5. Reaction scheme of complexes **1ad**–**1cf** with CO.

$N)(CO)(C(O)CH_3)]^+$ even though the ratio [BzQ]/[Pd] is 2.

In agreement with the in situ reactivity it was possible to isolate the acyl species $[Pd(phen)(py)(C(O)CH_3)]$-[OTf] (**2ad**) and $[Pd(phen)(2\text{-Ph-py})(C(O)CH_3)]$[OTf] (**2ae**), but not the BzQ derivatives (Scheme 5).

Therefore, the reactivity with CO of complexes **1ad**–**1cf** is different depending on the nature of the L ligand, which can be related to their Lewis basicity, which decreases on going from py to 2-Ph-py and to BzQ [35]. In agreement with the pK_{HB} trend, the acyl/acyl–carbonyl equilibrium is evident for the 2-phenyl-pyridine derivative, being, instead, totally shifted towards the acyl species for the pyridine one and towards the acyl–carbonyl for the benzoquinoline compound.

4. Conclusions

The complexes described above represent a development of the class of organometallic Pd(II) derivatives with two nitrogen-donor ligands bound to the same metallic centre. When both of the two N-ligands are bidentate molecules, one of them is coordinated in a unidentate fashion. Indeed, the crystal structure of one exponent of each series confirms the coordination of the monodentate N-ligand (either N-N behaving in this way or L) with its plane almost perpendicular to the square planar coordination plane.

A detailed ^1H and ^{15}N NMR investigation evidences the presence of a dynamic process in solution for the $[Pd(N\text{-}N)_2(CH_3)]^+$, which consists of alternate *flipping* and *opening–closure* processes, which exchange all the four nitrogen atoms. On the other hand the compounds $[Pd(N\text{-}N)(L)(CH_3)]^+$ do not show this kind of behaviour in solution and both their ^1H and ^{15}N NMR spectra confirm a non-symmetrical chemical environment for the N-N ligand.

For all these complexes the insertion of CO in the palladium–methyl bond is a very fast reaction leading to different products depending on the nature of the second molecule of N-ligand, which can compete with carbon monoxide for the fourth coordination site. It is straightforward to note that the decomposition of the palladium(II) species to metal was observed in any case.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 166125 and 166126 for complexes **1a** and **1ae**, respectively. Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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